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Multiferroics: a magnetic twist for ferroelectricity

Magnetism and ferroelectricity are essential to many forms of current technology, and the quest for multiferroic materials, where these two phenomena are intimately coupled, is of great technological and fundamental importance. Ferroelectricity and magnetism tend to be mutually exclusive and interact weakly with each other when they coexist. The exciting new development is the discovery that even a weak magnetoelectric interaction can lead to spectacular cross-coupling effects when it induces electric polarization in a magnetically ordered state. Such magnetic ferroelectricity, showing an unprecedented sensitivity to applied magnetic fields, occurs in 'frustrated magnets' with competing interactions between spins and complex magnetic orders. We summarize key experimental findings and the current theoretical understanding of these phenomena, which have great potential for tuneable multifunctional devices.

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In 1865, James Clerk Maxwell proposed four equations governing the dynamics of electric fields, magnetic fields and electric charges, which are now known as Maxwell's equations¹. They show that magnetic interactions and motion of electric charges, which were initially thought to be two independent phenomena, are intrinsically coupled to each other. In the covariant relativistic form, they reduce to just two equations for the electromagnetic field tensor, succinctly reflecting the unified nature of magnetism and electricity². A number of interesting parallels exist between electric and magnetic phenomena, such as the quantum scattering of charge off magnetic flux (Aharonov–Bohm effect³) and the scattering of magnetic dipoles off a charged wire (Aharonov–Casher effect⁴). The formal equivalence of the equations of electrostatics and magnetostatics in polarizable media explains numerous similarities in the thermodynamics of ferroelectrics and ferromagnets, for example their behaviour in external fields, anomalies at a critical temperature, and domain structures. These similarities are particularly striking in view of the seemingly different origins of ferroelectricity and magnetism in solids: whereas magnetism is related to ordering of spins of electrons in incomplete ionic shells, ferroelectricity results from relative shifts of negative and positive ions that induce surface charges.

Magnetism and ferroelectricity coexist in materials called multiferroics. The search for these materials is driven by the prospect of controlling charges by applied magnetic fields and spins by applied voltages, and using this to construct new forms of multifunctional devices. Much of the early work on multiferroics was directed towards

bringing ferroelectricity and magnetism together in one material⁵. This proved to be a difficult problem, as these two contrasting order parameters turned out to be mutually exclusive^{6–10}. Furthermore, it was found that the simultaneous presence of electric and magnetic dipoles does not guarantee strong coupling between the two, as microscopic mechanisms of ferroelectricity and magnetism are quite different and do not strongly interfere with each other^{11,12}.

The long-sought control of electric properties by magnetic fields was recently achieved in a rather unexpected class of materials known as 'frustrated magnets', for example the perovskites RMnO_3 , RMn_2O_5 (R: rare earths), $\text{Ni}_3\text{V}_2\text{O}_8$, delafossite CuFeO_2 , spinel CoCr_2O_4 , MnWO_4 , and hexagonal ferrite $(\text{Ba,Sr})_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ (refs 13–20). Curiously, it is not the strength of the magnetoelectric coupling or high magnitude of electric polarization that makes these materials unique; in fact, the coupling is weak, as usual, and electric polarization is two to three orders of magnitude smaller than in typical ferroelectrics. The reason for the high sensitivity of the dielectric properties to an applied magnetic field lies in the magnetic origin of their ferroelectricity, which is induced by complex spin structures, characteristic of frustrated magnets^{15,21–27}. Recent reviews of this rapidly developing field can be found in refs 28–30. Here, we mainly focus on the relationship between magnetic frustration and ferroelectricity, discuss different types of multiferroic materials and mechanisms inducing electric polarization in magnetic states, and outline the directions of the future research in this field.

PROPER AND IMPROPER FERROELECTRICS

Why is it difficult to find materials that are both ferroelectric and magnetic^{8,10,31}? Most ferroelectrics are transition metal oxides, in which transition ions have empty *d* shells. These positively charged ions like to form 'molecules' with one (or several) of the neighbouring negative oxygen ions. This collective shift of cations and anions inside a periodic crystal induces bulk electric polarization. The mechanism of the covalent bonding (electronic pairing) in such molecules is the virtual hopping of electrons from the filled oxygen shell to the

Table 1 Classification of ferroelectrics

	Mechanism of inversion symmetry breaking	Materials
Proper	Covalent bonding between $3d^0$ transition metal (Ti) and oxygen	BaTiO ₃
	Polarization of $6s^2$ lone pair of Bi or Pb	BiMnO ₃ , BiFeO ₃ , Pb(Fe _{2/3} W _{1/3})O ₃
Improper	Structural transition	K ₂ SeO ₄ , Cs ₂ CdCl ₄
	'Geometric ferroelectrics'	hexagonal RMnO ₃
	Charge ordering	LuFe ₂ O ₄
	'Electronic ferroelectrics'	
	Magnetic ordering	Orthorhombic RMnO ₃ , RMn ₂ O ₅ , CoCr ₂ O ₄
	'Magnetic ferroelectrics'	

empty d shell of a transition metal ion. Magnetism, on the contrary, requires transition metal ions with partially filled d shells, as the spins of electrons occupying completely filled shells add to zero and do not participate in magnetic ordering. The exchange interaction between uncompensated spins of different ions, giving rise to long-range magnetic ordering, also results from the virtual hopping of electrons between the ions. In this respect the two mechanisms are not so dissimilar, but the difference in filling of the d shells required for ferroelectricity and magnetism makes these two ordered states mutually exclusive.

Still, some compounds, such as BiMnO₃ or BiFeO₃ with magnetic Mn³⁺ and Fe³⁺ ions, are ferroelectric. Here, however, it is the Bi ion

with two electrons on the $6s$ orbital (lone pair) that moves away from the centrosymmetric position in its oxygen surrounding³². Because the ferroelectric and magnetic orders in these materials are associated with different ions, the coupling between them is weak. For example, BiMnO₃ shows a ferroelectric transition at $T_{FE} \approx 800$ K and a ferromagnetic transition at $T_{FM} \approx 110$ K, below which the two orders coexist¹². BiMnO₃ is a unique material, in which both magnetization and electric polarization are reasonably large^{12,33,34}. This, however, does not make it a useful multiferroic. Its dielectric constant ϵ shows only a minute anomaly at T_{FM} and is fairly insensitive to magnetic fields: even very close to T_{FM} , the change in ϵ produced by a 9-T field does not exceed 0.6%.

In the 'proper' ferroelectrics discussed so far, structural instability towards the polar state, associated with the electronic pairing, is the main driving force of the transition. If, on the other hand, polarization is only a part of a more complex lattice distortion or if it appears as an accidental by-product of some other ordering, the ferroelectricity is called 'improper'³⁵ (see Table 1). For example, the hexagonal manganites RMnO₃ (R = Ho–Lu, Y) show a lattice transition which enlarges their unit cell. An electric dipole moment, appearing below this transition, is induced by a nonlinear coupling to nonpolar lattice distortions, such as the buckling of R–O planes and tilts of manganese–oxygen bipyramids (geometric ferroelectricity)^{11,31,36}.

Another group of improper ferroelectrics, discussed recently, are charge-ordered insulators. In many narrowband metals with strong electronic correlations, charge carriers become localized at low temperatures and form periodic superstructures. The celebrated example is the magnetite Fe₃O₄, which undergoes a metal–insulator

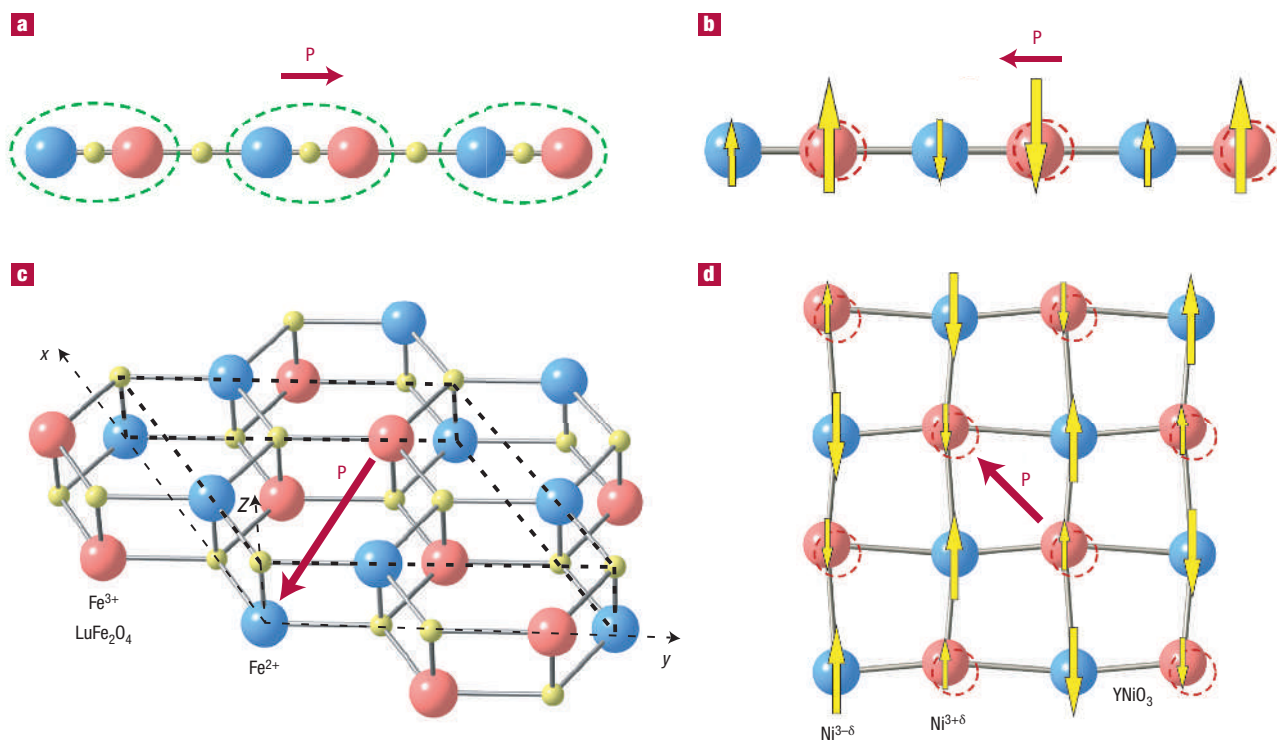


Figure 1 Ferroelectricity in charge-ordered systems. Red/blue spheres correspond to cations with more/less positive charge. **a**, Ferroelectricity induced by simultaneous presence of site-centred and bond-centred charge orders in a chain (site-centred charges and dimers formed on every second bond are marked with green dashed lines). **b**, Polarization induced by coexisting site-centred charge and $\uparrow\uparrow\downarrow\downarrow$ spin orders in a chain with the nearest-neighbour ferromagnetic and next-nearest-neighbour antiferromagnetic couplings. Ions are shifted away from centrosymmetric positions by exchange striction. **c**, Charge ordering in bilayered Lu(Fe^{2.5+})₂O₄ with a triangular lattice of Fe ions in each layer. The charge transfer from the top to bottom layer gives rise to net electric polarization. **d**, Possible polarization induced by charge ordering and the $\uparrow\uparrow\downarrow\downarrow$ -type spin ordering in the a – b plane of perovskite YNiO₃.

transition at ~ 125 K (the Verwey transition) with a rather complex pattern of ordered charges of iron ions³⁷. When charges order in a non-symmetric fashion, they induce electric polarization. It has been suggested that the coexistence of bond-centred and site-centred charge orders in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ leads to a non-centrosymmetric charge distribution and a net electric polarization³⁸ (see Fig. 1a). A polar lattice distortion induced by charge ordering has been reported in the bilayer manganite $\text{Pr}(\text{Sr}_{0.1}\text{Ca}_{0.9})_2\text{Mn}_2\text{O}_7$, which also shows an interesting reorientation transition of orbital stripes³⁹. Charge ordering in LuFe_2O_4 , crystallizing in a bilayer structure, also appears to induce electric polarization. The average valence of Fe ions in LuFe_2O_4 is 2.5+, and in each layer these ions form a triangular lattice. As suggested in ref. 40, the charge ordering below ~ 350 K creates alternating layers with $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratios of 2:1 and 1:2, inducing net polarization (see Fig. 1c).

FERROELECTRICITY IN FRUSTRATED MAGNETS

Naturally, improper ferroelectricity puts lower constraints on the coexistence with magnetism. In fact, materials with electric dipoles induced by magnetic ordering are the best candidates for useful multiferroics, because such dipoles are highly tuneable by applied magnetic fields. The current revolution in the field of multiferroics began with the discovery of the high magnetic tuneability of electric polarization and dielectric constant in the orthorhombic rare-earth manganites $\text{Tb}(\text{Dy})\text{MnO}_3$ and $\text{Tb}(\text{Dy})\text{Mn}_2\text{O}_5$ (refs 13,14,41,42). The onset of ferroelectricity in TbMnO_3 clearly correlates with the appearance of spiral magnetic ordering at ~ 28 K (ref. 43). In applied magnetic fields, $\text{Tb}(\text{Dy})\text{MnO}_3$ shows a spin-flop transition, at which the polarization vector rotates by 90° (see Fig. 2a) and the dielectric constant ϵ (in DyMnO_3) increases

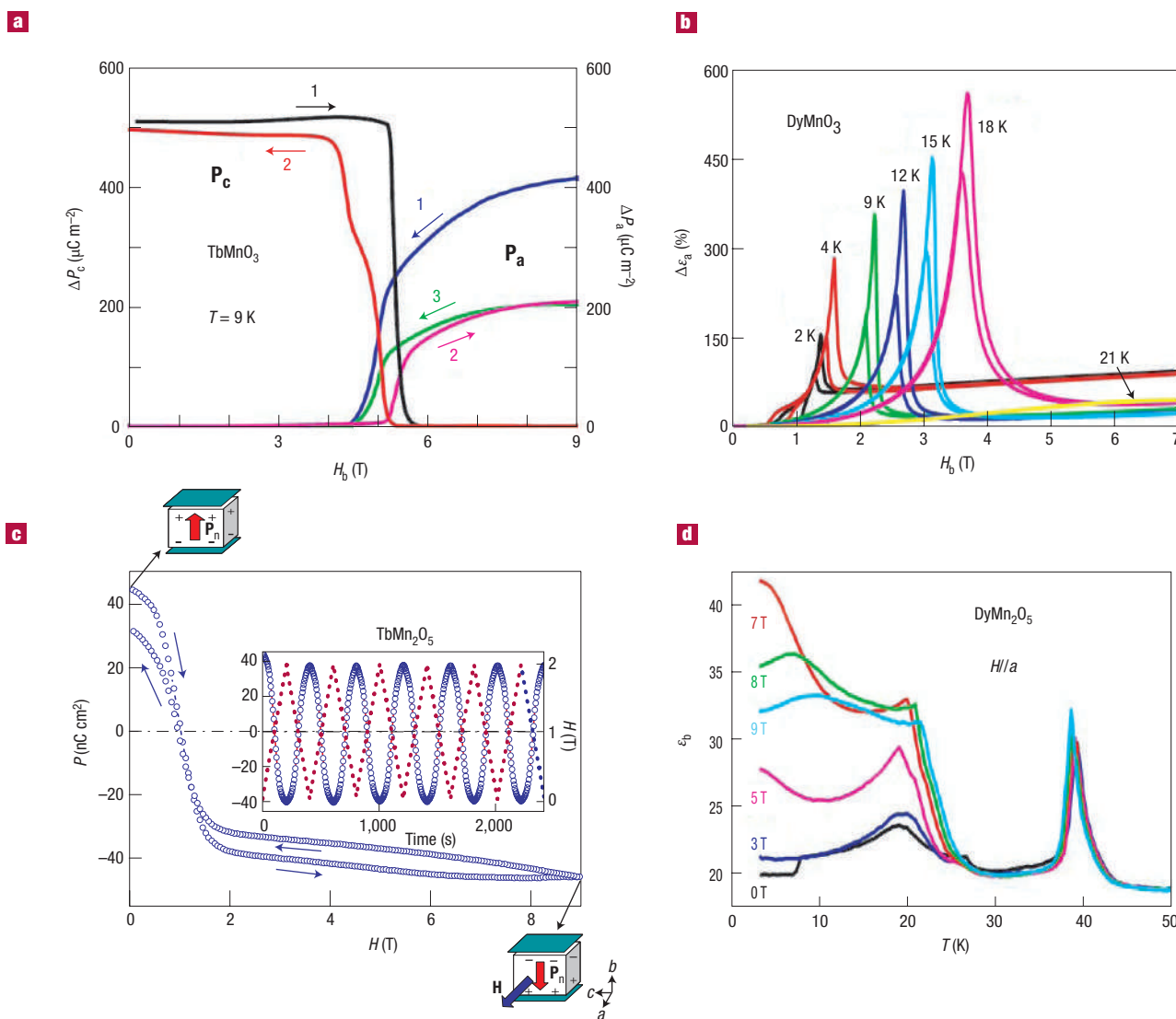


Figure 2 High magnetic tunability of magnetic ferroelectrics. **a**, Electric polarization in perovskite TbMnO_3 versus magnetic field along the b axis¹³. The magnetic field of ~ 5 T flips the direction of electric polarization from the c axis to the a axis. Numbers show the sequence of magnetic field variation. **b**, Dielectric constant ϵ along the a axis versus magnetic field along the b axis at various temperatures in perovskite DyMnO_3 . The sharp peak in $\epsilon(H)$ accompanies the flipping of electric polarization from the c axis to a axis. **c**, The highly reversible 180° flipping of electric polarization along the b axis in TbMn_2O_5 can be activated by applying magnetic fields along the a axis¹⁴. **d**, The temperature dependence of ϵ along the b axis in DyMn_2O_5 in various magnetic fields. The magnitude of the step-like increase of ϵ below ~ 25 K is strongly field-dependent. Parts **b** and **d** are reprinted with permission from refs 42 and 41, respectively. Copyright (2004) APS.

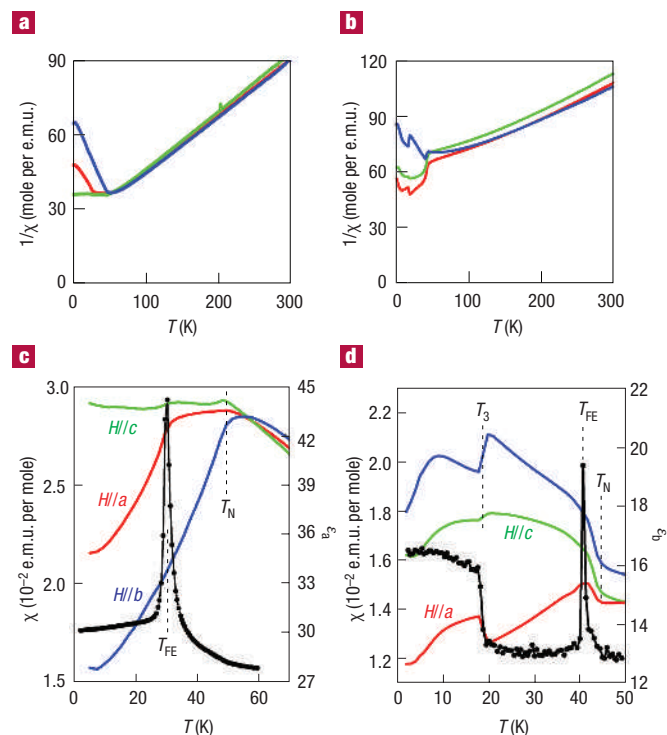


Figure 3 Temperature dependence of the inverse magnetic susceptibility of magnetically frustrated materials. **a**, $(\text{Eu}_{0.75}\text{Y}_{0.25})\text{MnO}_3$ and **b**, YMn_2O_5 both have magnetic transition temperatures (T_N) significantly lower than the corresponding Curie–Weiss temperatures. **c, d**, Anisotropic magnetic susceptibility as well as the dielectric constant along the ferroelectric polarization direction for $(\text{Eu}_{0.75}\text{Y}_{0.25})\text{MnO}_3$ (**c**) and YMn_2O_5 (**d**). The sharp peak of the dielectric constant curve indicates the onset of a ferroelectric transition. The data show that in $(\text{Eu}_{0.75}\text{Y}_{0.25})\text{MnO}_3$, the collinear magnetic state with the magnetic easy b axis is paraelectric, whereas the one with the easy a – b plane (magnetic spiral) is ferroelectric with electric polarization along the a axis. In ferroelectric YMn_2O_5 , spins have tendency to orient along the a axis, but rotate slightly from the a axis to the b axis on cooling at the temperature at which the dielectric constant shows a step-like increase. (Data are from Y. J. Choi, C. L. Zhang, S. Park and S.-W. Cheong, manuscript in preparation.)

by ~500% in a narrow field range. This colossal magneto-dielectric effect is shown in Fig. 2b.

Many of the rare-earth manganites RMn_2O_5 , where R denotes rare earths from Pr to Lu, Bi and Y, show four sequential magnetic transitions: incommensurate sinusoidal ordering of Mn spins at $T_1 = 42$ – 45 K, commensurate antiferromagnetic ordering at $T_2 = 38$ – 41 K, re-entrance transition into the incommensurate sinusoidal state at $T_3 = 20$ – 25 K, and finally, an ordering of rare-earth spins below $T_4 \leq 10$ K (refs 44–49). Ferroelectricity sets in at T_2 and gives rise to a peak in ϵ at this magnetic transition (see Fig. 3d). Furthermore, ϵ in DyMn_2O_5 shows a remarkably strong dependence on magnetic fields below T_3 (see Fig. 2d)⁴¹. The magnetic field rotates the electric polarization of TbMn_2O_5 by 180° in a highly reversible way¹⁴, as shown in Fig. 2c.

Complex magnetic structures and phase diagrams are observed in all multiferroics showing strong interplay between magnetic and dielectric phenomena^{13–20}. All these materials are ‘frustrated’ magnets, in which competing interactions between spins preclude simple magnetic orders. The disordered paramagnetic phase in frustrated magnets extends to unusually low temperatures. For example, the Curie–Weiss temperature, T_{CW} , of YMn_2O_5 , obtained by fitting its

magnetic susceptibility χ with the high-temperature asymptotic, $\chi \approx C/(T + T_{\text{CW}})$, is ~250 K (see Fig. 3b). The temperature T_{CW} reflects the strength of interaction between spins, and in usual magnets it gives a good estimate of the spin ordering temperature. The fact that the long-range magnetic order sets in at $T_1 \approx 45$ K, which is about five times smaller than T_{CW} , is clear indication for the presence of significant magnetic frustration in YMn_2O_5 .

HOW MAGNETIC SPIRALS INDUCE FERROELECTRICITY

The key questions are how it is possible that magnetic ordering can induce ferroelectricity and what the role of frustration is. The coupling between electric polarization and magnetization is governed by the symmetries of these two order parameters, which are very different. The electric polarization \mathbf{P} and electric field \mathbf{E} change sign on the inversion of all coordinates, $\mathbf{r} \rightarrow -\mathbf{r}$, but remain invariant on time reversal, $t \rightarrow -t$. The magnetization \mathbf{M} and magnetic field \mathbf{H} transform in precisely the opposite way: spatial inversion leaves them unchanged, whereas the time reversal changes sign. Because of this difference in transformation properties, the linear coupling between (\mathbf{P}, \mathbf{E}) and (\mathbf{M}, \mathbf{H}) described by Maxwell’s equations is only possible when these vectors vary both in space and in time: for example, spatial derivatives of \mathbf{E} are proportional to the time derivative of \mathbf{H} and vice versa.

The coupling between static \mathbf{P} and \mathbf{M} can only be nonlinear. Nonlinear coupling results from the interplay of charge, spin, orbital and lattice degrees of freedom. It is always present in solids, although it is usually weak. Whether it can induce polarization in a magnetically ordered state crucially depends on its form. A small energy gain proportional to $-P^2M^2$ does not induce ferroelectricity, because it is overcompensated by the energy cost of a polar lattice distortion proportional to $+P^2$. This fourth-order term accounts for small changes in dielectric constant below magnetic transition, observed for example in YMnO_3 and BiMnO_3 (refs 11,12). If magnetic ordering is inhomogeneous (that is, \mathbf{M} varies over the crystal), symmetries also allow for the third-order coupling of $PM\partial M$. Being linear in P , arbitrarily weak interaction of this type gives rise to electric polarization, as soon as magnetic ordering of a proper kind sets in. For cubic crystals, the allowed form of the magnetically induced electric polarization is^{22,23,26}

$$\mathbf{P} \propto [(\mathbf{M} \cdot \partial)\mathbf{M} - \mathbf{M}(\partial \cdot \mathbf{M})]. \quad (1)$$

This is where frustration comes into play. Its role is to induce spatial variations of magnetization. The period of magnetic states in frustrated systems depends on strengths of competing interactions and is often incommensurate with the period of crystal lattice. For example, a spin chain with a ferromagnetic interaction $J < 0$ between neighbouring spins has a uniform ground state with all parallel spins. An antiferromagnetic next-nearest-neighbour interaction $J' > 0$ frustrates this simple ordering, and when sufficiently strong, stabilizes a spiral magnetic state (see Fig. 4a):

$$\mathbf{S}_n = S [\mathbf{e}_1 \cos Qx_n + \mathbf{e}_2 \sin Qx_n], \quad (2)$$

where \mathbf{e}_1 and \mathbf{e}_2 are two orthogonal unit vectors and the wavevector Q is given by

$$\cos(Q/2) = -J'/(4J).$$

Like any other magnetic ordering, the magnetic spiral spontaneously breaks time-reversal symmetry. In addition it breaks inversion symmetry, because the change of the sign of all coordinates inverts the direction of the rotation of spins in the spiral. Thus, the symmetry of the spiral state allows for a simultaneous

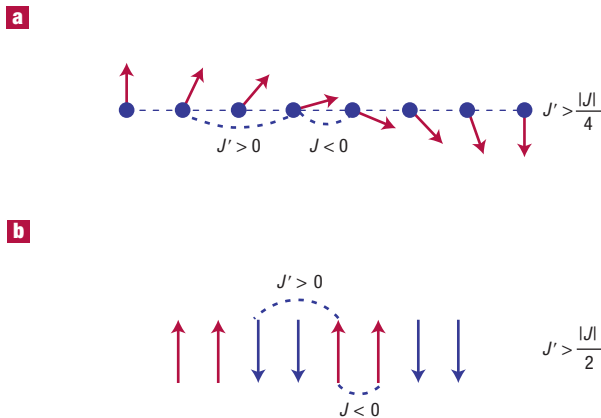


Figure 4 Frustrated spin chains with the nearest-neighbour FM and next-nearest-neighbour AFM interactions J and J' . **a**, The spin chain with isotropic (Heisenberg) $H_i = \sum_n [J \mathbf{S}_n \cdot \mathbf{S}_{n+1} + J' \mathbf{S}_n \cdot \mathbf{S}_{n+2}]$. For $J'/|J| > 1/4$ its classical ground state is a magnetic spiral. **b**, The chain of Ising spins $\sigma_n = \pm 1$, with energy $H_i = \sum_n [J \sigma_n \sigma_{n+1} + J' \sigma_n \sigma_{n+2}]$ has the up–up–down–down ground state for $J'/|J| > 1/2$.

presence of electric polarization, the sign of which is coupled to the direction of spin rotation. In contrast, a sinusoidal spin-density-wave ordering, $\mathbf{S}_n = \mathbf{S} \cos Qx_n$, cannot induce ferroelectricity, as it is invariant on inversion, $x_n \rightarrow -x_n$. Because magnetic anisotropies are inevitably present in realistic materials, the sinusoidal ordering usually appears at a higher temperature than the spiral one, which is why in frustrated magnets the temperature of ferroelectric transition is typically somewhat lower than the temperature of the first magnetic transition^{15,25,26}.

Spiral states are characterized by two vectors: the wavevector \mathbf{Q} and the axis \mathbf{e}_3 around which spins rotate. In the example considered above, \mathbf{Q} is parallel to the chain direction, and the spin-rotation axis $\mathbf{e}_3 = \mathbf{e}_1 \times \mathbf{e}_2$. Using equation (1), we find that the induced electric dipole moment is orthogonal both to \mathbf{Q} and \mathbf{e}_3 :

$$\mathbf{P} \parallel \mathbf{e}_3 \times \mathbf{Q} \quad (3)$$

A plausible microscopic mechanism inducing ferroelectricity in magnetic spirals was discussed in refs 24 and 27. It involves the antisymmetric Dzyaloshinskii–Moriya (DM) interaction, $\mathbf{D}_{n,n+1} \cdot \mathbf{S}_n \times \mathbf{S}_{n+1}$, where $\mathbf{D}_{n,n+1}$ is the Dzyaloshinskii vector^{50,51}. This interaction is a relativistic correction to the usual superexchange and its strength is proportional to the spin–orbit coupling constant. The DM interaction favours non-collinear spin ordering. For example, it gives rise to weak ferromagnetism in antiferromagnetic layers of La_2CuO_4 , the parent compound of high-temperature superconductors⁵² (see Fig. 5). It also transforms the collinear Néel state in ferroelectric BiFeO_3 into a magnetic spiral⁵³. Ferroelectricity induced by spiral magnetic ordering is the inverse effect, resulting from exchange striction: that is, lattice relaxation in a magnetically ordered state. The exchange between spins of transition metal ions is usually mediated by ligands, for example oxygen ions, forming bonds between pairs of transition metals. The Dzyaloshinskii vector $\mathbf{D}_{n,n+1}$ is proportional to $\mathbf{x} \times \mathbf{r}_{n,n+1}$, where $\mathbf{r}_{n,n+1}$ is a unit vector along the line connecting the magnetic ions n and $n+1$, and \mathbf{x} is the shift of the oxygen ion from this line (see Fig. 5). Thus, the energy of the DM interaction increases with \mathbf{x} , describing the degree of inversion symmetry breaking at the oxygen site. Because in the spiral state the vector product $\mathbf{S}_n \times \mathbf{S}_{n+1}$ has the same sign for all pairs of neighbouring spins, the DM interaction pushes negative oxygen ions in one direction perpendicular to the spin chain formed by positive

Effects of Dzyaloshinskii–Moriya interaction

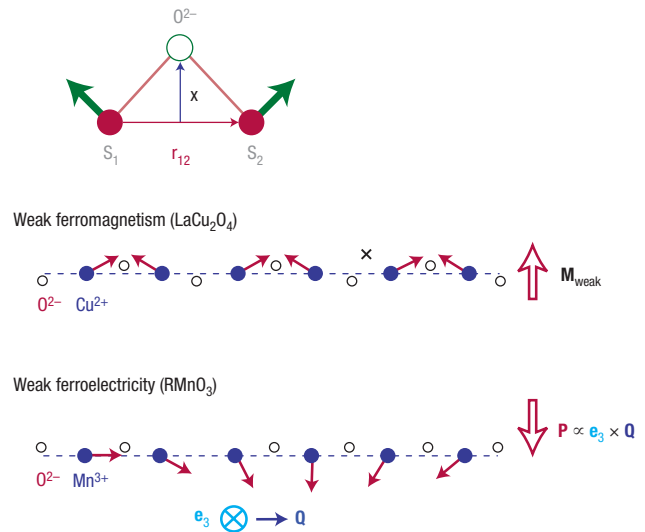


Figure 5 Effects of the antisymmetric Dzyaloshinskii–Moriya interaction. The interaction $H_{\text{DM}} = \mathbf{D}_{12} \cdot [\mathbf{S}_1 \times \mathbf{S}_2]$. The Dzyaloshinskii vector \mathbf{D}_{12} is proportional to spin–orbit coupling constant λ , and depends on the position of the oxygen ion (open circle) between two magnetic transition metal ions (filled circles), $\mathbf{D}_{12} \propto \lambda \mathbf{x} \times \hat{\mathbf{r}}_{12}$. Weak ferromagnetism in antiferromagnets (for example, LaCu_2O_4 layers) results from the alternating Dzyaloshinskii vector, whereas (weak) ferroelectricity can be induced by the exchange striction in a magnetic spiral state, which pushes negative oxygen ions in one direction transverse to the spin chain formed by positive transition metal ions.

magnetic ions, thus inducing electric polarization perpendicular to the chain²⁷ (see Fig. 5). This mechanism can also be expressed in terms of the spin current, $\mathbf{j}_{n,n+1} \propto \mathbf{S}_n \times \mathbf{S}_{n+1}$, describing the precession of the spin \mathbf{S}_n in the exchange field created by the spin \mathbf{S}_{n+1} . The induced electric dipole is then given by $\mathbf{P}_{n,n+1} \propto \mathbf{r}_{n,n+1} \times \mathbf{j}_{n,n+1}$ (ref. 24).

Although equation (3) works for many multiferroics (see discussion below), the general expression for magnetically induced polarization is more complicated. In particular, when the spin rotation axis \mathbf{e}_3 is not oriented along a crystal axis, the orientation of \mathbf{P} depends on strengths of magnetoelectric couplings along different crystallographic directions (such a situation occurs in MnWO_4 ; refs 18,19). Furthermore, when the crystal unit cell contains more than one magnetic ion, the spin-density-wave state, strictly speaking, cannot be described by a single magnetization vector, as was assumed in equation (1). With additional magnetic vectors, one can construct other third-order terms that can induce electric polarization. In this case, one can classify all possible spin-density-wave configurations according to their symmetry properties with respect to transformations that leave the spin-density-wavevector intact^{15,25}. According to the Landau theory of second-order phase transitions, close to transition temperatures the amplitudes of all spin configurations with the same symmetry should be proportional to a single order parameter. The sinusoidal phase is then described by one order parameter, whereas the ferroelectric state with additional broken symmetries is described by two order parameters, which are generalizations of the two orthogonal components of the simple spiral state.

SPIRAL MAGNETIC ORDER AND FERROELECTRICITY IN PEROVSKITE RMnO_3

These considerations explain the interplay between magnetic and electric phenomena observed in $\text{Tb}(\text{Dy})\text{MnO}_3$. Because of the orbital ordering of Mn^{3+} ions in orthorhombic RMnO_3 , the exchange between

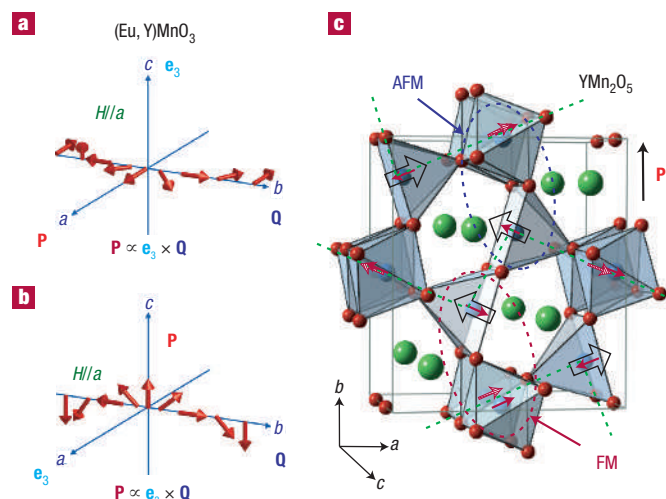


Figure 6 Spiral and non-spiral magnetic ferroelectrics. **a**, Spiral magnetic order in zero field with the spin rotation axis along the c axis and the wavevector along the b axis in $\text{Eu}_{0.75}\text{Y}_{0.25}\text{MnO}_3$, which breaks inversion symmetry and produces electric polarization along the a axis. **b**, The spin-flopped state in a magnetic field with the spin rotation axis along $H \parallel a$ and polarization along the c axis. **c**, Ordering of spins (red arrows) in the 'nearly collinear' phase of YMn_2O_5 . Green dashed lines indicate antiferromagnetic zigzags along the a axis. Large red and blue dotted ellipsoids indicate parallel and antiparallel spin pairs across the AFM zigzags, respectively. The antiferromagnetic nearest-neighbour spin coupling and exchange striction result in expansion/contraction of bonds connecting parallel/antiparallel spins. The resulting Mn^{3+} distortions, inducing the net electric polarization along the b axis, are shown with black open arrows. (The concepts in **a** and **b** are from Y. J. Choi, C. L. Zhang, S. Park and S.-W. Cheong, manuscript in preparation.)

neighbouring spins is ferromagnetic (FM) in the a - b planes and antiferromagnetic (AFM) along the c axis. Consistently, spins in each a - b plane of LaMnO_3 order ferromagnetically and the magnetization direction alternates along the c axis. The replacement of La by smaller ions such as Tb or Dy increases structural distortion, inducing next-nearest-neighbour AFM exchange in the a - b planes comparable to the nearest-neighbour FM exchange. This frustrates the FM ordering of spins in the a - b planes, and below ~ 42 K $\text{Tb}(\text{Dy})\text{MnO}_3$ shows an incommensurate magnetic ordering with a collinear sinusoidal modulation along the b axis, which is paraelectric. However, as temperature is lowered and magnetization grows in magnitude, a spiral state with rotating spins becomes energetically more favourable, sets in at ~ 28 K, and induces ferroelectricity⁴³. The wavevector \mathbf{Q} is parallel to b , and spins rotate around the a axis, which according to equation (3) induces \mathbf{P} parallel to the c axis, in agreement with experimental results. A similar transition from the paraelectric sinusoidal spin-density-wave state to the ferroelectric spiral state is observed¹⁵ in $\text{Ni}_3\text{V}_2\text{O}_8$.

The orientation of the polarization vector \mathbf{P} can be changed by applied magnetic fields. In zero or weak fields, spins rotate in the easy plane and thus the spin rotation axis \mathbf{e}_3 is parallel to the hard axis of a magnet. In strong fields, spins prefer to rotate around \mathbf{H} , which can force the spin-rotation axis to flop and induce a concomitant reorientation of \mathbf{P} . Such a 90° polarization flop was indeed observed^{13,54} in $\text{Tb}(\text{Dy})\text{MnO}_3$ at ~ 5 T. The low-temperature magnetic behaviour of these materials is, however, obscured by the fact that the rare-earth ions, Tb^{3+} and Dy^{3+} , which are also magnetic with a strong anisotropy, undergo their own spin-flop transitions in magnetic fields.

It is much easier to interpret the field-induced transitions in orthorhombic manganites with non-magnetic rare earth ions, such as

$\text{Eu}_{0.75}\text{Y}_{0.25}\text{MnO}_3$. As was already mentioned, the size of the rare earths in RMnO_3 is essential for the magnetic frustration, ferroelectricity as well as the stability of orthorhombic perovskite structure. Thus, orthorhombic RMnO_3 with $\text{R} = \text{La-Gd}$ does not show ferroelectricity, whereas for rare earths smaller than Dy, RMnO_3 crystallizes in the hexagonal YMnO_3 structure in ambient conditions. Desired physical properties can be obtained by mimicking the size of Tb(Dy) with an appropriate mixture of non-magnetic Eu and Y ions. For example, $\text{Eu}_{0.75}\text{Y}_{0.25}\text{MnO}_3$ has the orthorhombic perovskite structure and undergoes magnetic and ferroelectric transitions similar to those in $\text{Tb}(\text{Dy})\text{MnO}_3$. The temperature dependence of magnetic susceptibility χ of $\text{Eu}_{0.75}\text{Y}_{0.25}\text{MnO}_3$, shown in Fig. 3c, is consistent with an easy- b -axis sinusoidal state below ~ 50 K, and a magnetic spiral with the easy a - b plane below ~ 30 K. The magnetic spiral is ferroelectric with polarization along the a axis (the temperature dependence of ϵ_a is shown in Fig. 3c), presumably because \mathbf{Q} is parallel to b and \mathbf{e}_3 is parallel to c (Y. J. Choi, C. L. Zhang, S. Park and S.-W. Cheong, manuscript in preparation; and refs 55,56). For $H \parallel a$, Mn spins undergo the spin-flop transition and start rotating in the b - c plane around \mathbf{H} (see Fig. 6b). The flop from $\mathbf{e}_3 \parallel c$ to $\mathbf{e}_3 \parallel a$ results in the 90° rotation of the polarization vector \mathbf{P} from the a axis to the c axis.

Another interesting type of field-induced transition was found in the delafossite CuFeO_2 (ref. 16). In this material, magnetic Fe^{3+} ions form triangular layers and exchange interactions among spins are strongly frustrated. The magnetic anisotropy with the easy c axis aligns spins in the direction perpendicular to layers, and in the ground state they form a collinear state commensurate with the crystal lattice. A magnetic field of ~ 6 T, applied in the c direction, induces a spin-flop transition, which forces spins to form a spiral state and induces electric polarization in the a - b plane.

EXCHANGE STRICTION WITHOUT MAGNETIC SPIRALS

Spiral spin ordering is not the only possible source of magnetically induced ferroelectricity⁵⁷⁻⁶⁰. Electric polarization can also be induced by collinear spin orders in frustrated magnets with several species of magnetic ions, such as orthorhombic RMn_2O_5 with Mn^{3+} ions ($S = 2$) in oxygen pyramids and Mn^{4+} ions ($S = 3/2$) in oxygen octahedra. A view along the c axis (see Fig. 6c) reveals that Mn spins are arranged in loops of five spins: Mn^{4+} - Mn^{3+} - Mn^{3+} - Mn^{4+} - Mn^{3+} . The nearest-neighbour magnetic coupling in the loop is AFM, favouring antiparallel alignment of neighbouring spins. However, because of the odd number of spins in the loop, ordered spins cannot be antiparallel to each other on all bonds, which gives rise to frustration and favours more complex magnetic structures. Figure 6c shows the Mn spin configuration in the commensurate phase of RMn_2O_5 , which appears below T_2 and consists of AFM zigzag chains along the a axis (dashed green lines).

To understand how ferroelectricity can be induced by this (nearly) collinear magnetic state, we note that half of the Mn^{3+} - Mn^{4+} pairs across neighbouring zigzags have approximately antiparallel spins, whereas the other half have more-or-less parallel spins. The exchange striction shifts ions (mostly Mn^{3+} ions inside pyramids) in a way that optimizes the spin-exchange energy: ions with antiparallel spins are pulled to each other, whereas ions having parallel spins, despite the AFM exchange interaction, move away from each other. This leads to the distortion pattern shown with open black arrows in Fig. 6c, which breaks inversion symmetry (in particular, on oxygen sites connecting two Mn^{3+} pyramids) and induces net polarization along the b axis.

In the incommensurate magnetic phase below $T_3 = 20$ -25 K, the magnetization of the Mn ions in each zigzag chain is modulated along the a axis and spins in every other chain are rotated slightly toward the b axis. This behaviour is reflected in the temperature dependence of χ , showing a sudden increase and drop of χ along the a and b axes, respectively, at T_3 on cooling. This results in the reduction as well as the

180° rotation of the net ferroelectric distortion. To make things even more complicated, there also seems to be a net ferroelectric moment associated with the ordering of rare-earth spins, which is opposite to that induced by the incommensurate ordering of Mn ions (thus, in the same direction as that in the commensurate state). In TbMn_2O_5 at low temperatures, the net distortion associated with Tb spins is larger than that due to Mn spins, but disappears when Tb spins align along $H\parallel a$. This explains the 180° rotation of net polarization induced by magnetic fields at low temperatures.

A conceptually simpler example of how a collinear spin ordering can induce ferroelectricity is the frustrated spin chain with competing FM and AFM interactions, where spins can orient only up or down, as in the so-called ANNNI model⁶¹. A strongly frustrated Ising spin chain with nearest-neighbour ferromagnetic and next-nearest-neighbour antiferromagnetic coupling has the up–up–down–down ($\uparrow\uparrow\downarrow\downarrow$) ground state (see Fig. 4b). If the charges of magnetic ions or tilts of oxygen octahedra^{59,60} alternate along the chain, this magnetic ordering breaks inversion symmetry on magnetic sites and induces electric polarization (see Fig. 1b). As in the case of magnetic spirals, ions are displaced by exchange striction, which shortens bonds between parallel spins and stretches those connecting antiparallel spins in the $\uparrow\uparrow\downarrow\downarrow$ state. In the Landau description, the coupling term inducing the polarization has the form of $P(L_1^2 - L_2^2)$, typical for improper ferroelectrics^{35,60}, where $L_1 = S_1 + S_2 - S_3 - S_4$ and $L_2 = S_1 - S_2 - S_3 + S_4$ represent two possible types of the ($\uparrow\uparrow\downarrow\downarrow$) order. Similarly, the electric polarization in the RMn_2O_5 compounds is induced by the ($\uparrow\uparrow\downarrow\downarrow$) or ($\downarrow\downarrow\uparrow\uparrow$) spin ordering along the b axis, which has the same period as the alternation of the Mn charges (Mn^{3+} – Mn^{3+} – Mn^{4+}) along this axis. Because the lattice distortion in this mechanism is driven by the Heisenberg (rather than by the weak DM) exchange, the induced polarization can be large. It would be interesting to explore multiferroics in which ferroelectricity appears as a combined effect of charge and magnetic ordering that together break inversion symmetry. Note that site-centred charge ordering coexisting with the spin ordering of the up–up–down–down type has been observed in perovskites RNiO_3 (see Fig. 1d)^{62–64}.

WHERE TO GO FROM HERE?

Magnetic frustration is a powerful source of ‘unconventional’ magnetic orders, which can induce ferroelectricity. Particularly suited for magnetic control of polarization are conical magnets, such as the spinel CoCr_2O_4 (ref. 17), in which magnetization has both rotating and uniform ferromagnetic parts: $S_n = S_\perp[\mathbf{e}_1 \cos Qx_n + \mathbf{e}_2 \sin Qx_n] + S_\parallel \mathbf{e}_3$.

While the rotating part of the magnetization gives rise to ferroelectricity, the net ferromagnetic moment of the spiral provides a ‘handle’, with which the orientation of the spin rotation axis, and hence the polarization vector, can be tuned by applied magnetic fields. Magnetic fields required to reverse the orientation of electric polarization in CoCr_2O_4 are substantially lower than those in rare earth manganites. The simultaneous presence of electric polarization and net magnetization in the conical ferroelectric CoCr_2O_4 gives rise to an average toroidal moment $\langle \mathbf{T} \rangle \propto \langle \mathbf{P} \times \mathbf{M} \rangle$, which is parallel to the spiral wave vector and remains unchanged when \mathbf{P} and \mathbf{M} are rotated by low magnetic fields^{17,53}.

Unfortunately, the strong effects of magnetic fields on electric polarization and dielectric constant do not imply strong dependence of magnetic properties on applied electric fields, as magnetoelectric coupling in frustrated magnets is rather weak. Furthermore, as spontaneous electric polarization does not break time-reversal symmetry, it cannot induce magnetic ordering in the same way as a magnetic order with broken inversion symmetry induces ferroelectricity. To achieve control of magnetism by electric fields, one has to find other mechanisms, such as mutual clamping of ferroelectric

and antiferromagnetic domains, which appears to be relevant to a linear magnetoelectric effect in hexagonal HoMnO_3 (refs 65–67).

From a technological point of view, a challenge in this field is to find room-temperature multiferroics. As was mentioned above, magnetic frustration usually delays magnetic transitions down to low temperatures, so that finding high-temperature insulating spiral magnets is not straightforward (but not impossible — in the multiferroic hexaferrite $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$, spins order above room temperature²⁰). An alternative route is to artificially fabricate composite ferroelectric and magnetic materials with high transition temperatures. There have been considerable efforts to optimize the cross-coupling effects in composite multiferroics with magnetostrictive ferromagnets and piezoelectric materials^{68–70} (see also the accompanying review by Ramesh and Spaldin on page 21 of this issue⁷¹).

Equation (1) states that the polarization density is proportional to the gradient of the angle φ , describing the orientation of spins in the spiral: $P \propto \partial\varphi$. This has two immediate consequences: first, the total electric polarization is proportional to the total number of revolutions of spins in the spiral and is insensitive to the presence of higher harmonics, and second, Néel domain walls carry net electric polarization and magnetic vortices have electric charge^{22,26}. The 180° Néel wall separating spin-up and spin-down domains induces polarization, because it has electric properties of a half period of a magnetic spiral with $\mathbf{e}_3 \perp \mathbf{Q}$. On the other hand, the Bloch wall, where spins rotate around the normal to the wall, induces no net polarization, similar with the spiral with $\mathbf{e}_3 \parallel \mathbf{Q}$. The electric polarization induced by domain walls may be of practical importance, as domain walls can form in thin films of conventional ferromagnetic materials above room temperature and show very strong sensitivity to applied magnetic fields.

The coupling between electric and magnetic dipoles in multiferroics also gives rise to unusual dynamic effects, which can be observed in optical experiments^{21,72–74}. The salient feature of many proper ferroelectrics is the softening of optical phonons at the critical temperature, resulting in divergent ϵ (refs 6,9,75). The freezing of this soft mode below the transition temperature leads to a bulk ferroelectric distortion. In magnetic ferroelectrics, the soft mode seems to be absent despite the divergence of ϵ at the magnetic phase transition that induces electric polarization. The peak in ϵ in this case results from the linear coupling between the polar phonon mode and the soft magnetic mode. The mixing of magnetic excitations (magnons) with optical phonons and, eventually, with light makes it possible to ‘see’ magnons in optical absorption experiments. The photoexcitation of magnons also occurs in ordinary magnets, but there the single magnon excitation occurs only through magnetic dipole coupling of the light (known as magnetic resonance) and is much weaker than electric dipole excitations such as the optical phonons. On the other hand, in multiferroics the coupling can result from the third-order term $PM\partial M$. The linear coupling is obtained by replacing one vector \mathbf{M} by the static magnetization with the wavevector \mathbf{Q} of the magnetic structure, while another vector \mathbf{M} is replaced by the dynamic magnetization with the wavevector $-\mathbf{Q}$. This coupling induces significant ‘magnetic’ peaks in the optical absorption spectrum. The theory of the coupled spin-phonon excitations (‘electro-magnons’) was discussed in the 1970s and more recently in ref. 76. Since then, a few reports have appeared on the absorption peaks at frequencies typical for magnetic excitations, most recently^{77–79} in the spiral magnets $\text{Tb}(\text{Gd})\text{MnO}_3$. Still, dynamic phenomena in multiferroics remain largely unexplored and require future work.

In summary, magnetic frustration naturally gives rise to multiferroic behaviour. Competing magnetic interactions in frustrated magnets often result in eccentric magnetic structures that lack the inversion symmetry of a high-temperature crystal lattice. The ionic relaxation in such magnetic states, driven by lowering of the magnetic energy

of the Heisenberg and Dzyaloshinskii–Moriya exchange interactions, induces polar lattice distortions. These magnetic ferroelectrics can produce unprecedented cross-coupling effects, such as the high tuneability of the magnetically induced electric polarization and dielectric constant by applied magnetic fields, which has given a new impulse to the search for other multiferroic materials and raised hopes for their practical applications.

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